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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

MODIFICATIONS OF HEMPEL'S GAS-APPARATUS.

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The object of this paper is the description of some simple devices which make possible the accurate analysis of gases with a minimum of special apparatus.

I. Absorbing Pipette.

The essential feature of Hempel's method is the use of simply constructed vessels distinct from the measuring burette for the purpose of absorbing successively the various constituents of a gaseous mixture. Hempel used for this end a modification of Ettling's gas pipette, which answers the purpose admirably; but of course many other combinations of apparatus might be used. The simplest is perhaps a bulb or wide tube inserted over liquid contained in a bottle. In order to prevent the access of air into this bulb from below, it is well to make the lower part of the tube somewhat narrow, and to bend it upward. If desired, the capillary serving to admit the gas may be bent downwards and then upwards, as it is in the Hempel pipette; but with intelligent use of the pinchcock this precaution is not necessary. A satisfactory form of the apparatus is illustrated in Figure 1.

Fifty cubic centimeters is quite enough gas for analysis, if a suitably narrow burette is used for measurement, hence the receiving bulb of the pipette (A) need not exceed seventy-five cubic centimeters in capacity. The bottle (C) should be capable of holding one hundred and fifty cubic centimetres in this case.

The "compound pipette" of Hempel may be imitated by the addition at B of another bottle containing water and a levelling funnel, or the same object may be attained merely by connecting to the outlet B a flexible rubber bulb, such as a child's toy balloon.

For solids, the stem D of the pipette may be made of wider tubing, closed at the bottom with a perforated stopper. A small tube bent upwards may be inserted in this perforation, if especial precaution against incoming air is desired.

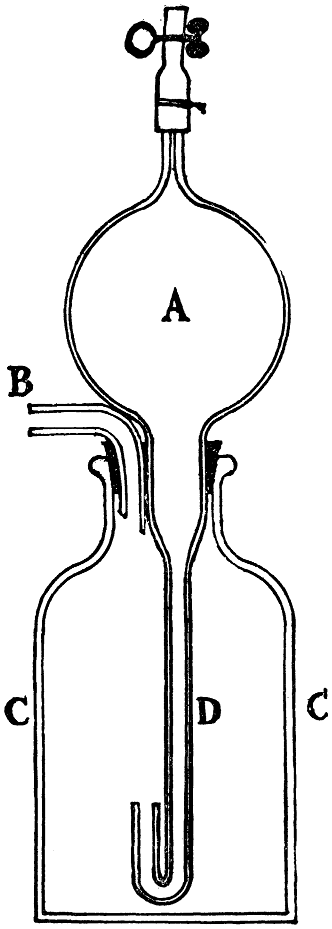

Figure 1.

An explosion-pipette could be made of similar apparatus, with the addition of a stopcock just below the bulb A and the usual conducting wires.

The pipette for fuming acid might be made with a ground-glass joint instead of a stopper to connect bulb with bottle. In that case the bottle should be provided with a suitable side tube on the neck, bent upwards.

The method of using these pipettes will be understood without difficulty by any one familiar with the Hempel apparatus.

II. Measuring Apparatus.

The most serious cause of error in Hempel's ordinary apparatus is due to the possible change of temperature. This is considerably greater than the probable error in reading; for a single degree Celsius causes an error of 0.5 per cent of the total volume of gas measured under ordinary conditions, while the volume is easily read within 0.05 per cent. Hence, unless much greater care than usual is taken to preserve constant temperature, the reading of the volume is unnecessarily precise. But Hempel's ingenious arrangements for maintaining constant conditions in a 100 c.c. burette are so large as to be inconvenient for students' use in cramped quarters.

For these reasons I have often used somewhat smaller volumes, which may be surrounded with an envelope of water without producing thereby an unwieldy combination. An ordinary 50 c. c. burette, inverted and provided with a levelling bulb or funnel, answers very well as a measuring instrument. The burette may even be used in its usual position, if it is provided above with a smooth rubber stopper with a single hole for the capillary connecting-tube. Of course the stopper is always pushed precisely into a definite position, indicated by a carefully made mark on the burette. There is little risk of displacing this stopper if it is firmly wired into place. In any case of course the ungraduated space at the upper extremity must be carefully calibrated. An especially made 50 c.c. instrument, graduated all the way to the capillary tube at the top, is more convenient, although no more accurate than the inverted burette. For convenience in cleaning, it is well not to have both ends of the burette drawn down to small diameter. The small size of the burette makes it easily possible to provide the water jacket which is so essential for accurate work, and both burette and pipette may be supported upon the ordinary iron ring stand.

III. Practical Operation.

Of course the precautions usually necessary in gas analysis must be used in all the operations with this apparatus. For example, due time must be allowed for the running down of the liquid from the moistened walls. Again, care must be taken that the same amount of gas, at definite pressure (as small an amount as possible) is always left in the connecting capillary tubes. In order to make sure that no air-bubbles are caught, it is well to draw out the ends of the tubes in the manner illustrated in the diagram, which indicates two successive stages of the glass blowing, as well as the finished and connected nipple. The object of blowing the small bulbs is to render the bore of the portions drawn out as large as that of the rest of the tube.

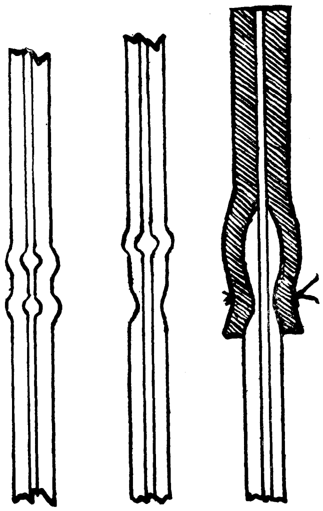

Figure 2.

While the apparatus thus constituted was devised primarily for use in an emergency, it has several advantages over the Hempel apparatus. It dispenses with the necessity of calibrating the whole length of a new burette, it is very inexpensive, and it occupies but little space. Each student may possess a complete set of apparatus, and every one knows the value from a pedagogic standpoint of such a possibility. A further advantage lies in the fact that the pipette is easy to fill and to clean; and a precipitate in the liquid is not apt to clog its working. The short straight capillary brings an obvious gain of speed in transferring. Moreover, because of this speed, and the fact that the pressure during transferrence is always from the outside inward, the danger of loss by leakage is considerably less than it is with Hempel's apparatus. It is well known that in a rubber tube an internal pressure may cause leakage, while an external pressure tends to stop small outlets by causing the rubber tube to be pressed more closely together.

On the other hand, the calculation is less obvious, because the volume taken is not just a hundred cubic centimeters; and somewhat more care must be used to prevent the access of air into the pipette from below while shaking. A little practice enables one to shake thoroughly the liquid in the bulb without much agitation in the bottle if the movement is hinged about the point D; hence the danger is slight. Another slight difficulty is the possible leakage of the absorbent around the stopper of the pipette bottle, — an unpleasant occurrence which has no effect upon the accuracy of the method.

In presenting for general use any new instrument one must record its practical working in the laboratory. Everybody knows that plausible

Analysis of known Mixtures of Air and Carbon Dioxide.

Volume CO_2 taken.	Volume Air taken.	Volume Air found.	Error.
c. c.	c. c.	c. c.	c. c.
16.95	32.02	32.01	–0.01
18.45	32.21	32.12	–0.09
12.20	42.20	42.20	±0.00
20.00	32.00	32.10	+0.10
14.90	37.60	37.60	±0.00
13.00	34.50	34.48	–0.02
16.50	36.50	36.55	+0.05
Excess of positive over negative errors, 0.03.			

inventions do not always stand the test of indiscriminate use. Accordingly a large class in gas analysis has been asked to use the new devices, with favorable outcome.

The pipette and burette were tested as follows. A definite amount of air was run into the burette, and the volume measured with the usual care. Pure carbon dioxide was then run in from a generator, and the gain in volume was noted. This known mixture of air and carbon dioxide was run over into the new pipette, and after suitable shaking the residual air was returned to the burette and measured.

These figures, taken at random from among the results of the class, agree with one another as well as could be expected; and since the positive deviation balances the negative, there is no constant error. No trouble was experienced as to manipulation.

I am much indebted to Mr. Bisbee, the assistant, and to the gentlemen of the class in gas analysis, for their kindness in carrying out the practical trial of the apparatus.

CAMBRIDGE, May 3, 1901.